COAL TAR AND PETROLEUM PITCHES AS BINDERS FOR SODERBERG ELECTRODES

L. F. King
W. D. Robertson

Research Department, Imperial Oil Enterprises Ltd, Sarnia, Ontario, Canada

INTRODUCTION

It was concluded from a previous study[1] that the efficacy of coal tar and petroleum pitches as binders for coke in carbon electrodes is governed mainly by their aromaticity and content of distillable coke precursors. A thermal petroleum pitch containing about the same amount of resins insoluble in quinoline and benzene as coal tar pitch, but no volatile coke formers, was unsatisfactory as an electrode binder[2]. On the other hand, a vacuum reduced residue from a petroleum catalytic cracking process, though having no C_1 (quinoline insoluble) or C_2 (quinoline soluble, benzene insoluble) resins and few of the other characteristics of coal tar pitch, generally gave laboratory test electrodes having high density and compressive strength.

Parameters affecting the yield of binder pitch from the petroleum catalytic cracking process have been identified. Data obtained by vacuum reduction of catalytically cracked residues are shown in Figure 1. The yield of pitch having a softening point of 95°C is a function of aromaticity, as indicated by the U.S. Bureau of Mines Correlation Index (BMCI), the yield increasing from 6% of an 80 BMCI residue to 30% of a 120 BMCI residue. Figure 2 shows the relationship between aromaticity of the material boiling above 370°C and cracking severity as indicated by feed conversion to gas and naphtha boiling below 221°C.

In aluminum manufacture, inorganic contaminants in either the binder or coke aggregate components of the electrodes in the reduction furnace may show up as impurities in the product, or may accumulate in the molten electrolyte and reduce the current efficiency of the cell. Typical specifications for electrode binder pitches allow a maximum of 0.3% ash. To meet this requirement, it is necessary to remove at least 95% of the catalyst fines (corresponding to all particles larger than about 10 microns) from catalytically cracked residue. Semi-commercial studies showed that this can be accomplished by allowing the solids to settle in tankage at 65°-110°C for 5-10 days per foot of liquid depth.

EXPERIMENTAL

Some Soderberg pastes made with cracked petroleum pitch are mechanically unstable at high temperatures: at 255°C oil components are exuded from the green mix of pitch and petroleum coke aggregate. This was found to be a function of binder content, separation of oil being observed only at the pitch level required to impart adequate flow properties to the paste. Oil bleeding is an undesirable property because of the possibility of leakage from the anode casing in commercial operation. A related phenomenon is a tendency for the green mix to decrease in consistency soon after preparation. Mechanical instability is not normally observed when paste is prepared with coal tar pitch as binder.

Earlier work had indicated that a pitch suitable as an electrode binder could be made by heat soaking a catalytically cracked petroleum residue at about 375°C in the presence of an active carbon catalyst (type CAL, 12-40 mesh, Pittsburgh Coal and Chemical Co. Inc.)[3] and the yield also was increased from 25% to 42%. Though it was well known that coarse (thermal) carbon blacks, when added in large quantities to Soderberg paste, may act as a replacement for some of the coke fines[4], the use of catalytic amounts of high surface area, non-pelletized blacks pre-dispersed in the pitch had not been reported.

The type of carbon black is critical[5]. The most suitable ones are the super abrasion (SAF) furnace blacks, intermediate super abrasion (ISAF), semi-reinforcing (SRF) furnace blacks made by G. L. Cabot Inc. and fast extruding furnace black (FEF) of Columbian Carbon Co. Because of their high surface area, structural characteristics and surface adsorption properties, these rubber reinforcing grade blacks are also effective as stabilizers for Soderberg paste (Table 1). At a concentration of 5% in catalytically cracked petroleum binder (1.5% of the paste) the furnace blacks prevented bleeding of oil and change in consistency of the green mix, whereas the large particle size MT (thermal) black provided no significant improvement in these properties. It is probable that there is also a catalytic effect involving the formation of C_1 and C_2 resins in situ during the carbonization (baking) process. It is important to note that, to be effective, aggregates in commercial pelletized carbon blacks must be broken down into discrete particles. A concentrated suspension of the black in an aromatic distillate (from thermal cracking of gas oil), prepared by mixing in a tank, was passed through a colloid mill, and a quantity sufficient to give the desired carbon black content in the finished binder was blended with the vacuum reduced pitch or with the feedstock to distillation. The blending oil was removed later in vacuo.

When proper dispersion is attained, there is little or no tendency for solids to settle out of pitches containing furnace blacks during hot storage. Frequent circulation of coal tar electrode binder pitch is commonly practiced in the industry to minimize the deposition of benzene and quinoline insoluble components in storage tanks. One micron is reported as the average diameter of quinoline insolubles[6]. Our laboratory data showed that two representative coal tar pitches deposited about half of their C_1 and C_2 resins in 5 to 20 days at 205°C. A cracked petroleum pitch, in which 5% of pelletized SRF black (80 mμ particle diameter) had been dispersed by colloid milling, required 330 days at 225°C for settling of 25% of the black.

Flow Properties of Soderberg Pastes

In addition to its other functions, the binder in Soderberg paste must impart the fluidity necessary for flow to all parts of the anode casing. This depends on the gradation of the coke aggregate (which in practice is fixed), the amount of binder and its viscosity.

The flow properties of Soderberg paste are commonly evaluated by an empirical "elongation" test[3,5]. Four samples of paste, pressed into a cylindrical mold and cooled rapidly, are placed on an aluminum test plate - made so that the surface is sloped at an angle of 10° to the horizontal - and heated in an oven at 255°C for 15 minutes. The plate is then removed from the oven, shock chilled, and the elongation of the samples as a percentage of the original length is calculated. For commercial electrodes, the value desired is approximately 100%, and it varies more or less logarithmically with the binder content. With coal tar pitches, 30 to 35% binder is needed[7].

Although the addition of a small amount of furnace black to a binder substantially improves the stability of Soderberg paste, it also reduces fluidity. Typical results for two such carbon blacks in catalytically cracked petroleum pitch are shown in Figure 3. Elongation also depends on the particle size of the black (Figure 4). Thermal blacks have a negligible effect on paste fluidity at low concentrations; this is undoubtedly related to their inability to modify the oil bleeding and aging characteristics of the paste.

A study was made of the flow properties of catalytically cracked petroleum pitches containing SRF carbon black and of Soderberg paste made with them. An experimental sample, designated as "Cracked Pitch D" was prepared on a small commercial scale as described above. Another pitch (Blended Pitch E) was prepared in the laboratory. Vacuum reduced (480°C+) bottoms from catalytic cracking, blended with 5 wt % of a 150°C softening point vacuum reduced tar from thermal cracking of gas oil, and a dispersion of SRF carbon black in oil were redistilled in vacuo to remove the oil. These two petroleum pitches are compared in Table 2 with a coal tar pitch binder (F) typical of that used at about 30% concentration in Soderberg paste.

The viscosity of electrode binder pitch is normally measured with a Brookfield viscosimeter at various temperatures and spindle rotation speeds. The rate of shear is high, but not precisely known. This is not important in the case of coal tar pitches which are reported to be Newtonian[8]. Since cracked petroleum pitches were suspected of being pseudoplastic, it was decided to determine viscosity at known shear rates.

Flow properties of binders D, E and F were evaluated in Koppers vacuum capillary viscometers at three temperatures: 107, 135 and 163°C. Data obtained at various shear rates are shown in Figures 5, 6 and 7. While coal tar pitch F was confirmed as being Newtonian throughout, the petroleum pitches were shear sensitive. At the lowest temperature and shear rate D had the lowest viscosity, at 135°C it was intermediate and at 163°C and high shear rate it had the lowest viscosity. Flow indices calculated for D and E were 0.7 and 0.9 (1.0 for F).

In commercial practice, Soderberg paste is cast into blocks about 3.5 x 13 x 1 ft in size and weighing over 5000 lb. The anodes are replenished by placing a block of solidified paste on top, where the temperature is 100-150°C. The paste should flow to all corners of the anode casing under these conditions. The pressure at the bottom of a block of paste due to its own weight is approximately 10^4 dynes/cm^2. The laboratory elongation test previously described was developed to control the fluidity of Soderberg pastes made with coal tar pitch under average commercial operating conditions. In the laboratory test, the stress causing the paste to flow is about 10^3 dynes/cm^2 but the temperature (225°C) seemed much too high. Additional elongation tests done at 205° and 150°C gave the results shown in Figure 8. The binder requirements of the three pitches were as indicated, being based on 80-100% elongation at 255°C. The effect of too little binder on the elongation of the paste is shown by the lowest curve.

To simulate the very low shear rates of commercial operation, a laboratory spreading test was developed. A block of Soderberg paste, 1.5 x 6 x 0.5 inches in size and loaded with steel weights as required, is placed in a shallow steel container (2.5 x 6 x 0.25 inches) and heated in an oven at 150°C. Since the volume of the container was made equal to the volume of the semi-molten block of paste, spreading of the block is complete when the container is filled. Tests were carried out using pastes containing the "optimum" amount of coal tar pitch F, cracked pitch D, and blended pitch E, for periods of 1, 8 and 16 hours: (a) under a load of 0.5 psi which produces a stress of about 10^4 dynes/cm^2, and (b) under no applied load. The results are shown in Figure 9.

Correlations between Soderberg paste elongation, spreading tests and the apparent viscosity of the binder under similar conditions of temperature and stress are complex. At 255°C and a shearing stress of 10^3 dynes/cm^2, the apparent viscosities of all three binders tested are so low (0.01 poise) that the binder viscosity probably has little effect on the flow properties of the paste. Under these conditions, it is the amount of binder that has the greatest effect on the fluidity of the paste by controlling the packing of the coke aggregate particles.

In the elongation test at 150°C, there is some indication that the flow of the paste increases as the apparent viscosity of the binder increases, and the same result was observed in the spreading test at 150°C under a load of 0.5 psi (upper curve, Figure 10). It is possible that in this viscosity range (about 1 to 10 poises) the film of binder on the coke aggregate particles is not of sufficient thickness to lubricate them under a stress of 10^3 to 10^4 dynes/cm^2; and as the viscosity of the binder is increased, friction between the particles decreases due to the thicker lubricant film.

In the spreading test at 150°C with no applied load (lower curve, Figure 10) flow varies directly as the apparent viscosity of the binder, indicating that at extremely low stress levels, the viscous resistance of the binder has a significant retarding effect on the flow of the paste.

Electrode Performance

The performance of the binders in laboratory scale baked electrodes is summarized in Table 3. The procedure of Jones et al was used[9]. All test data appear satisfactory. For cracked pitch D, the optimum binder content, the elongation at 225°C immediately after preparation and again after aging the paste for 24 hr at 225°C, and the properties of baked test electrodes made from aged and unaged paste are given.

L. Girolami[10] has reported a "saturation" test which involves heating coal tar Soderberg paste in two stages (at 200°C and at 300°C) prior to laboratory coking at the normal temperature of 550°C. The yield of coke was increased by the preheating steps, depending on the fineness of the coke, the soaking temperature and the binder/aggregate ratio. Girolami ascribed this behaviour to displacement of air or other gases adsorbed on the coke aggregate, thus permitting more intimate contact between binder and coke. Our results appear to confirm this finding: the density and compressive strength of electrodes increased significantly after heat soaking of the paste. This has been observed in our laboratory with many petroleum pitches.

A small scale trial of cracked petroleum pitch D was carried out in a commercial Soderberg anode. In spite of the fact that less than the indicated optimum amount of binder was inadvertently used in the paste (26 vs 31%) the performance was satisfactory, the rate of anode consumption being low. The paste on the top of the cell required manual spreading since it would not spread to fill the casing completely by virtue of its own weight. The petroleum binder exhibited extremely low volatility at the ambient temperature, so the amount of vapour above the cell was almost negligible compared to that evolved by coal tar binders.

Upgrading Coal Tar Pitch

Coal tar pitches from different sources are variable in quality. Low grade binders can be improved for Soderberg electrode use by addition of furnace blacks in much the same way as petroleum residua. The improvement is evidenced by increased density and compressive strength of baked test electrodes. Coal tar pitches which are most readily upgraded are those having a relatively low coking value (about 50%) and a quinoline insolubles content of less than 10%. Literature data[6] indicate that the best coal tar binders contain 10 to 15 wt % of quinoline insoluble resins.

Laboratory inspections and performance data are summarized in Table 4. Addition of 2.5 wt % of a reinforcing black to poor quality coal tar pitches effected a marked improvement in performance. In one case, (A), the elongation of the paste was below the desired value for Soderberg electrodes, but this could be overcome by increasing slightly the amount of binder used. This is shown in B, where the retarding effect of the carbon black on paste flow was compensated for by increasing the binder content from 30.5 to 32%.

ACKNOWLEDGEMENT

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EFFECT OF AROMATICITY OF CATALYTIC FRACTIONATOR RESIDUE ON THE YIELD OF PITCH

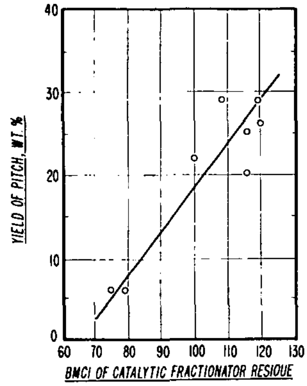

Figure 1

EFFECT OF CATALYTIC CRACKING SEVERITY ON THE AROMATICITY OF FRACTIONATOR RESIDUE

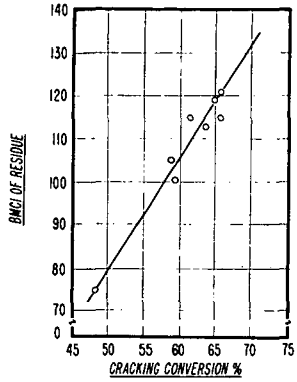

Figure 2

PROPERTIES OF SODERBERG PASTES

BINDER	Coal Tar Pitch (Typical)	Catalytically Cracked Petroleum Pitch				
CARBON BLACK IN BINDER						
TYPE	None	None	- Furnace -			Thermal
GRADE			ISAF	SRF	SRF	MT
AVER PARTICLE SIZE, mμ			23	80	80	470
WT			2.5	5.0	7.5	5.0
OPTIMUM BINDER CONTENT, WT. %	28-33	27	31	32	33	30
STABILITY	Good	Poor	Good	Good	Good	Poor
AGEING CHARACTERISTICS	Good	Poor	Poor	Good	Good	Poor
BAKED TEST ELECTRODE COMPRESSIVE STRENGTH, Kg/cm^2	250-450	270-405	400	380	410	370

Table 1

EFFECT OF CARBON BLACK CONCENTRATION IN CRACKED PETROLEUM PITCH ON FLOW PROPERTIES OF SODERBERG PASTE

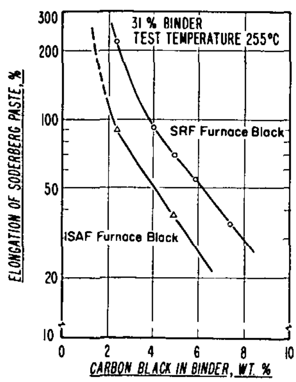

Figure 3

EFFECT OF PARTICLE SIZE OF CARBON BLACK IN CRACKED PETROLEUM PITCH BINDER ON THE FLOW PROPERTIES OF SODERBERG PASTE

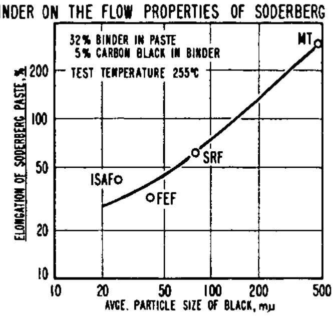

Figure 4

PROPERTIES OF BINDERS FOR SODERBERG ELECTRODES

	Coal Tar Pitch	Petroleum Pitch	
COMPOSITION, WT. %	F	D	E
VACUUM REDUCED CAT CRACKING RESIDUE		95	90
VAC REDUCED THERMAL CRACKING RESIDUE		–	5
SRF CARBON BLACK		5	5
PROPERTIES			
SOFTENING POINT (C/A) °C	92	90	92
DENSITY AT 15°C. g/cm³	1.31	1.23	1.24
COKING VALUE, WT. %	56	54	57
BENZENE INSOLUBLE, WT. %	22	9	10
QUINOLINE INSOLUBLE, WT. %	10	6	7

Table 2

APPARENT VISCOSITY
OF
ELECTRODE BINDER PITCHES AT 107°C

KOPPERS TYPE VACUUM CAPILLARY VISCOMETER

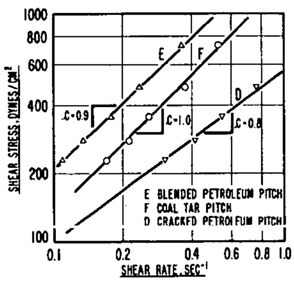

Figure 5

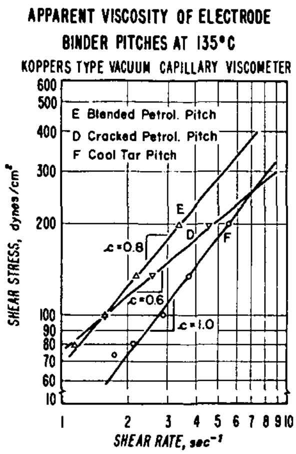

Figure 6

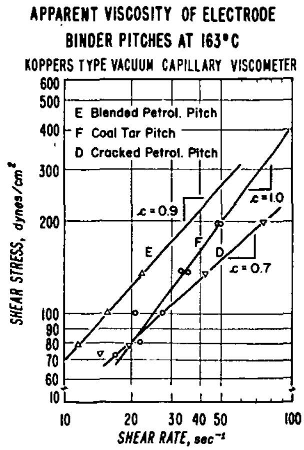

Figure 7

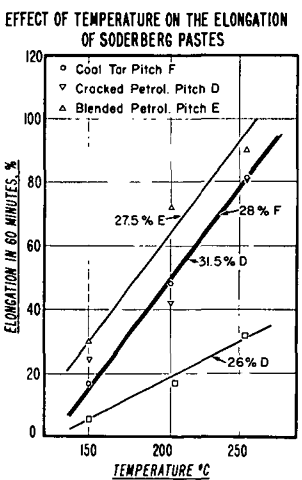

Figure 8

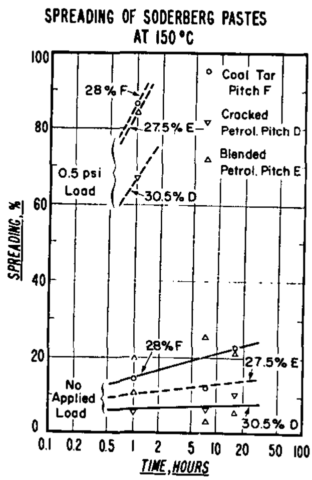

Figure 9

COAL TAR AND PETROLEUM PITCHES AS BINDERS FOR SODERBERG ELECTRODES

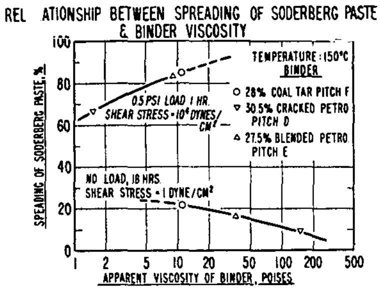

Figure 10

PERFORMANCE OF SODERBERG ELECTRODE BINDERS

Binder	Coal Tar Pitch F	Petroleum Cracked Pitch D			Petroleum Blended Pitch E
SODERBERG PASTE					
BINDER CONTENT, WT. %	28	29	31	33	27.5
ELONGATION AT 255°C, %	80	40	64	181	72
AFTER AGEING	–	57	92	174	–
BAKED ELECTRODES					
DENSITY, g/cc					
FROM UNAGED PASTE	1.42	1.44	1.43	1.40	1.39
FROM AGED PASTE [1]	–	–	1.47	1.46	–
COMPRESSIVE STRENGTH, Kg/cm^2					
FROM UNAGED PASTE	354	372	361	288	313
FROM AGED PASTE [1]	–	–	424	403	–

(1) 24 HR. AT 225°C.

Table 3

UPGRADING COAL TAR BINDERS BY ADDITION OF CARBON BLACK

PITCH	A		B	
CARBON BLACK	NONE	2.5% ISAF	NONE	2.5% SAF
SOFTENING POINT, °C	--- 92 ---		--- 110 ---	
COKING VALUE, %	50	53	51	53
BENZENE INSOLUBLES, %	25	28	24	28
QUINOLINE INSOLUBLES, %	6	9	2	6
SODERBERG PASTE				
BINDER, %	30.5	30.5	30.5	32
ELONGATION, % (255°C)	78	32	60	59
BAKED ELECTRODES				
APPARENT DENSITY, g/cm^3	1.38	1.45	1.38	1.41
COMPRESSIVE STRENGTH, Kg/cm^2	295	434	274	386

Table 4